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Bis(piperidinium) tetrachlorozincate

Adrian Fowkes and William T. A. Harrison*

Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland

Correspondence e-mail: w.harrison@abdn.ac.uk

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Key indicators

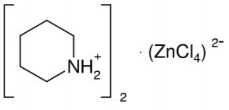
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.030
wR factor = 0.072
Data-to-parameter ratio = 32.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $(C_5H_{12}N)_2[ZnCl_4]$, contains a network of piperidinium cations and tetrahedral $(ZnCl_4)^{2-}$ [d_{av}(Zn—Cl) = 2.2725 (6) Å] anions. The crystal packing is influenced by cation-to-anion N—H···Cl hydrogen bonds (three simple and one bifurcated), resulting in a structure with layered character.

Comment

The title compound, (I) (Fig. 1), complements recently reported salt-like associations between (protonated) amines and anionic metal–chloride polyhedra, such as $(C_6H_{14}N_2)[CuCl_4]$ and $(C_6H_{14}N_2)[CuCl_4]\cdot H_2O$ (Wei & Willett, 2002), and $(C_6H_{14}N_2)[CoCl_4]$ (Bremner & Harrison, 2003). The energetics of N—H···Cl—M (M = metal) hydrogen bonds and their possible role as synthons in supramolecular chemistry have been described in detail by Brammer *et al.* (2002).



(I)

The structure of (I) contains two distinct $C_5H_{12}N^+$ piperidinium cations and a tetrahedral $[ZnCl_4]^{2-}$ anion. The organic species adopt typical chair conformations and their geometrical parameters [d_{av}(C—N) = 1.484 (3) Å and d_{av}(C—C) = 1.504 (3) Å] are similar to those of the same cation in piperidinium chloride, $(C_5H_{12}N)Cl$ (Gaudet *et al.*, 1989). The $[ZnCl_4]^{2-}$ group in (I) with d_{av}(Zn—Cl) = 2.2725 (6) Å is typical (Viossat *et al.*, 1984).

As well as electrostatic attractions, the component species in (I) interact by means of a network of N—H···Cl links (Table 2). There are three simple N—H···Cl links

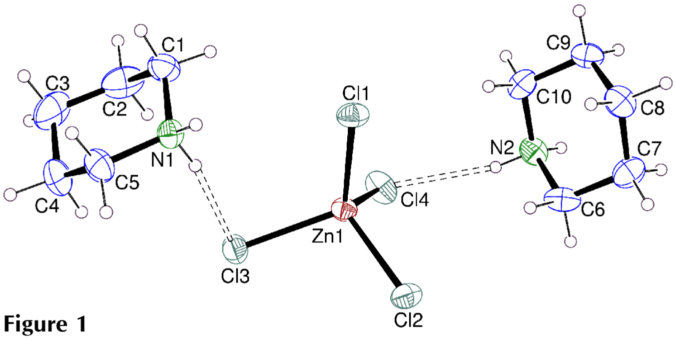


Figure 1
The asymmetric unit of (I) (50% displacement ellipsoids). H atoms are drawn as small spheres of arbitrary radius and hydrogen bonds are indicated by dashed lines.

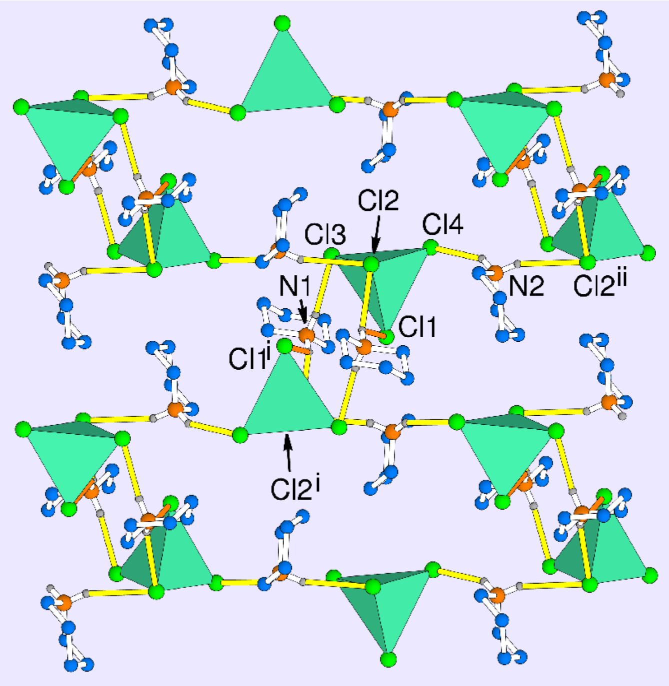


Figure 2
Detail of a hydrogen-bonded sheet in (I). Colour key: $[ZnCl_4]^{2-}$ tetrahedra green, Cl atoms green, C atoms blue, N atoms orange and H atoms grey. The H···Cl portions of the N—H···Cl hydrogen bonds with $d < 2.7$ Å and $d > 2.7$ Å are highlighted in yellow and orange, respectively. Symmetry labels as in Table 2 (atom $Cl2^{i}$ is hidden behind a solid tetrahedron).

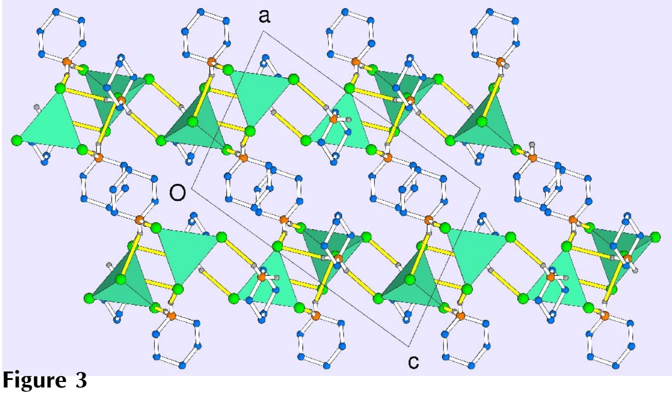


Figure 3
[010] projection of (I). The colour key is as in Fig. 2, except that all H···Cl bonds are highlighted in yellow.

[d_{av}(H···Cl) = 2.45 Å; d_{av}(N···Cl) = 3.307 (2) Å; θ_{av}(N—H···Cl) = 160°] and one bifurcated N1—H2···($Cl1^{i}$,$Cl2^{i}$) bond (see Table 2 for symmetry code), with the two acceptor chloride ions forming a tetrahedral edge. One of the H···Cl contacts is long (2.86 Å) in this case and was flagged as being of questionable significance in a *PLATON* (Spek, 2003) analysis of the structure. However, the Cl1···Cl2 separation of 3.5959 (7) Å is significantly less than the average of the other Cl···Cl distances [3.7306 (8) Å] and the donor–acceptor bond-angle sum about H2 is 351°, suggesting that this bond is weak, but not merely a packing artifact. By comparison, the N—H···Cl bonds [d_{av}(H···Cl) = 2.06 (1) Å] to the 'bare' chloride ion in $(C_5H_{12}N)Cl$ (Gaudet *et al.*, 1989) are much stronger than any of the hydrogen bonds seen in (I), which is consistent with results of the database survey of Aullón *et al.* (1998) into hydrogen bonds to chloride or metal-bound chloride acceptors. The H···Cl—Zn bond angles (Table 1; average angle = 93°) are typically acute, which can be related to a simple bonding model (Aullón *et al.*, 1998) in which the chloride *p*-type lone pairs are more basic than the *sp*-type lone pair.

The organic and inorganic species interact so as to generate a $(10\overline{1})$ hydrogen-bonded sheet (Fig. 2). This may be decomposed into pairs of $[ZnCl_4]^{2-}$ tetrahedra which are linked by pairs of N1-containing piperidinium cations, the whole assemblage being generated by inversion symmetry [d(Zn···Zn^{i}) = 6.0840 (4) Å]. These pseudo-clusters are crosslinked by the N2-containing piperidinium cations, resulting in layers extended throughout the crystal structure [d(Zn···Zn^{ii}) = 8.1865 (5) Å]. Finally, the interleaved neutral $(10\overline{1})$ sheets interact by way of van der Waals forces (Fig. 3), resulting in a layered structure.

Experimental

The following aqueous solutions were mixed at 293 K in a Petri dish: 4 ml of 1 *M* piperidine, 2 ml of 1 *M* zinc chloride, and 4 ml of 1 *M* HCl. This resulted in a clear solution and colourless block-like crystals of (I) grew as the water evaporated at 293 K over the course of a few days.

Crystal data

$(C_5H_{12}N)_2[ZnCl_4]$
$M_r = 379.48$
Monoclinic, $P2_1/n$
$a = 9.6583$ (4) Å
$b = 12.0849$ (5) Å
$c = 14.9557$ (7) Å
$\beta = 101.470$ (1)°
$V = 1710.76$ (13) Å^3
$Z = 4$
$D_x = 1.473$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5271 reflections
$\theta = 2.3$–30.0°
$\mu = 2.04$ mm^{-1}
$T = 293$ (2) K
Block, colourless
0.36 × 0.28 × 0.16 mm

Data collection

Bruker SMART1000 CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{min} = 0.516$, $T_{max} = 0.721$
13983 measured reflections
4972 independent reflections
3588 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 30.0°$
$h = -13 \rightarrow 13$
$k = -15 \rightarrow 17$
$l = -21 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.072$
$S = 0.97$
4972 reflections
154 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0376P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.64$ e Å^{-3}
$\Delta\rho_{min} = -0.45$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—Cl4	2.2508 (5)	Zn1—Cl3	2.2812 (6)
Zn1—Cl1	2.2722 (5)	Zn1—Cl2	2.2858 (5)
Zn1—Cl1···$H2^{i}$	81	Zn1—Cl3···H1	90
Zn1—Cl2···$H2^{i}$	90	Zn1—Cl4···H14	111
Zn1—Cl2···$H13^{ii}$	91		

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N1—H1⋯Cl3	0.90	2.33	3.2146 (16)	169
N1—H2⋯Cl2$^{\rm i}$	0.90	2.50	3.2459 (15)	141
N1—H2⋯Cl1$^{\rm i}$	0.90	2.86	3.4764 (14)	127
N2—H13⋯Cl2$^{\rm iii}$	0.90	2.64	3.4912 (19)	158
N2—H14⋯Cl4	0.90	2.39	3.215 (2)	153

Symmetry codes: (i) $-x, 1-y, 1-z$; (iii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.

All H atoms were placed in idealized positions [d(C—H) = 0.97 Å and d(N—H) = 0.90 Å] and refined as riding, with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(parent atom).

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97; molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *ATOMS* (Shape Software, 1999); software used to prepare material for publication: *SHELXL*97.

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